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The main structural units in silicate materials are silica and alumina tetrahedra that are linked together by bridging oxygen atoms to form complex chains, sheets, and three-dimensional networks. Most studies of silicate structures focus on these $(Al,Si)O_x$ polymer units, and the degree of interlinking between them. Another important aspect, however, that is more difficult to determine, is the degree of association of other cations with the polymer units. The phase diagrams of many simple binary and ternary oxide systems seem to suggest that this association can be substantial. Diffusive isotopic fractionation of major cations in silicate liquids may also provide information on the association of cations with the polymer units, and perhaps on the effective size of the polymer units. The isotopic species should diffuse at different rates depending on the mass of the diffusing species, and the extent of isotopic fractionation by diffusion may indicate the size of the polymer unit associated with each ion and/or the degree of association between the cations and the polymer structure. We are approaching this problem using binary diffusion couples with rhyolite liquid on one side and mafic liquid on the other, run in piston cylinder apparatus for several hours at 1450°C and 1 GPa. This follows the experiments of Richter et al. (2003), who demonstrated significant isotopic fractionation for Ca and Li isotopes in silicate liquids with natural chemical compositions. Those experiments show that diffusive fractionation of Ca isotopes is small when considering the elemental mass ratio (44/40), as if Ca is associated with larger polymer units. In contrast, Li isotopes exhibit a much greater diffusive fractionation that suggests the diffusing species are comparable in size to the elemental masses. As noted by Richter et al., the bulk diffusivity of Li is very high and similar to that of hydrogen. Presumably Li, like H, is not strongly bound to the silicate polymer units and is readily exchanged between units, allowing for both fast diffusion and greater mass discrimination. We have reproduced the results of Richter et al. (2003) for Ca isotopes using rhyolite and tholeiitic basalt. As in their experiments, we see significant Ca isotope fractionation (ca. 6 per mil) that can be reproduced in models of chemical diffusion using different diffusivities for the ^{40}Ca and ^{44}Ca species. However, we also observe isotopic gradients in the charges that are not accounted for in our model of chemical diffusion. We have repeated the experiment with a mafic liquid (ugandite) of different composition, which has lower silica activity, higher Mg and alkalis, and is presumably less polymerized than tholeiitic basalt. Preliminary results indicate that the degree of Ca isotopic fractionation varies with composition, and that there are large isotopic effects in our experimental charges that may be due to temperature gradients and/or tracer diffusion in addition to simple chemical diffusion.

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